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RESEARCH MEMORANDUM

APPLICATION OF AN ULTRAVIOLET SPECTROPHOTOMETRIC
METHOD TO THE ESTIMATION OF ALKYLNAPHTHALENES
IN 10 EXPERIMENTAL JET-PROPULSION FUELS

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RESEARCH MEMORANDUM

APPLICATION OF AN ULTRAVIOLET SPECTROPHOTOMETRIC

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SUMMARY

A means of using the strong absorption by alkyl-naphthalenes in the range from approximately 2500 to 2700 A to check estimates of the concentrations based on spectrophotometric measurements at about 3150 A has been devised and applied to 10 experimental jet-propulsion fuels that are petroleum cuts boiling in the range from 100° to 700° F (approximately 40° to 400° C). The 10 fuels investigated are one Yates, three Hastings, two Tomball, two Bradford, and two Midway crude cuts. This check procedure involved empirically determining the average characteristic extinction at 2650 A most suitable for alkyl-naphthalenes in these fuels and estimating the amount of other aromatics, which were largely monocyclic. Sums of amounts of alkyl-naphthalenes and of other aromatics constituted spectrophotometric estimates for total aromatics. Differences between those estimates and values for total aromatics in the same samples obtained at the Petroleum Experiment Station, Bureau of Mines, Bartlesville, Oklahoma, by a silica-gel adsorption method were recognized to be due to several causes including interfering absorption, erroneous estimates of the amounts of other aromatics, and small inaccuracies of the Bartlesville data. Nevertheless these differences were tentatively attributed entirely to errors in spectrophotometric estimates of alkyl-naphthalenes in order to establish an upper value for the order of magnitude of these errors, which was computed to be about 0.2 percent of total sample. In this manner the spectrophotometric method for estimation of alkyl-naphthalenes was shown to be more accurate than was formerly expected and some additional information concerning the composition of the fuels was obtained. The possibility of undetectable interference, however, prevents proposal of ultraviolet estimation of total aromatics as an independent method except in particular cases.

INTRODUCTION

The combustion efficiencies of 10 experimental jet-propulsion fuels that are approximately 200° F cuts of five selected crudes available in large quantities are being determined in a turbojet engine combustor at altitude conditions at the NACA Cleveland laboratory. These fuels are as follows:

Crude	Approximate boiling range (°F)
Yates	160-340
Hastings	120-310
Hastings	280-400
Hastings	410-690
Tomball	210-340
Tomball	400-590
Bradford	90-360
Bradford	340-540
Midway	110-390
Midway	370-630

These determinations are part of a program investigating the effects of fuel composition on performance in jet combustors at sea level and at altitude. (See reference 1.) Extensive data on the physical characteristics and the chemical composition of these 10 experimental fuels in terms of hydrocarbon types were obtained from the Petroleum Experiment Station, Bureau of Mines, Bartlesville, Oklahoma. The values for total aromatics included in these data have been assumed to be correct because they were obtained by a silica-gel adsorption method (reference 2), which is one of the most reliable methods currently available.

Alkyl-naphthalenic aromatics are characterized by absorption in the range from approximately 2500 to 2700 Å, which is much more intense than either the absorption near 3150 Å or the absorption by monocyclic aromatics at 2650 Å. Hence, the method described for estimating total aromatics, which is based on average characteristic absorption by these two types of aromatic at 2650 Å, is very sensitive to variations in the value for the alkyl-naphthalenic content. The purpose of this investigation is to take advantage of this magnification of errors in alkyl-naphthalenic estimates to investigate the accuracy of the spectrophotometric method of estimation of

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alkylnaphthalenic hydrocarbons proposed in reference 3. The investigation consisted in determining differences between spectrophotometric estimates and the previously mentioned accepted values for total aromatics in the 10 experimental fuels and then computing the order of magnitude of errors in alkylnaphthalenic estimates that would have caused these differences. The absorption at selected wavelengths in the ultraviolet spectra of the fuels and of several aromatics that have boiling points ranging from 150° to 350° C was measured at the Cleveland laboratory and average characteristic extinctions at 2650 Å most suitable for application to these fuels were evaluated empirically using the spectra of reference 4 and other unpublished data. Information concerning the alkylnaphthalenic and total aromatic content of the fuels was a byproduct of the investigation.

PRINCIPLES OF SPECTROPHOTOMETRIC ANALYSIS AND

DESCRIPTION OF METHOD

Method for Alkylnaphthalenes

The ultraviolet spectrophotometric method for estimation of alkylnaphthalenic type hydrocarbons in kerosenes described in reference 3 proposed an average value of about 8 for E_0D_0 , the product of extinction measured at a peak of absorption between 3100 and 3300 Å and dilution factor (defined as volume of solution divided by volume of solute). The number 8 is the characteristic value of E_0D_0 for a 1 percent by volume solution in isooctane of typical alkylnaphthalenes in an absorption cell 0.5 centimeter thick (for 100-percent alkylnaphthalenes the value of E_0D_0 was 800 in reference 3). Division of the product of extinction and dilution factor by 8 for the higher peak between 3100 and 3300 Å of a petroleum cut dissolved in isooctane and measured in a 0.5-centimeter cell is essentially the method of reference 3 for estimating percent by volume of alkylnaphthalenic hydrocarbons C_N . Paraffins, naphthenes, olefins, alkylbenzenes, and noncondensed dicyclic compounds would not interfere with this estimate but subtraction of the extinction of the diluted petroleum cut measured at 3400 Å before further calculations was recommended as a correction for possible interference by condensed tricyclic and other possible interfering compounds that have absorption throughout the range from 3100 to 3400 Å.

Method for Total Aromatics

Nearly all aromatics are characterized by absorption in the vicinity of 2650 A and average absorption by alkylnaphthalenic compounds is from 10 to 20 times as intense as the average absorption by alkylbenzenes and noncondensed nonconjugated dicyclics at this wavelength. An ultraviolet-spectrophotometric method for estimating the total aromatic content of cuts of crude oil may therefore be established according to the principles of reference 4 on the basis of suitable average characteristic extinctions of the aromatics expected to be present. The cuts are assumed to be mixtures of the two ultraviolet-absorbing components, alkylnaphthalenes and other aromatics, which are largely monocyclic, dissolved in ultraviolet-transparent paraffins, naphthenes, and olefins. Absorption at 2650 A is the sum of the absorption by both component types. This sum may be represented mathematically by the equation

$$ED = C_N k_1 + C_A k_2$$

where

- C_N concentration of alkylnaphthalenic aromatics, percentage by volume
- C_A concentration of monocyclic and other aromatics, percentage by volume
- D dilution factor, which is the ratio of volume of solution to volume of solute
- k_1 average specific extinction of alkylnaphthalenes at 2650 A
- k_2 average specific extinction of monocyclic and other aromatics at 2650 A
- E extinction of properly diluted sample of cut measured at a selected wavelength (2650 A in this case)

The specific extinctions must be estimated as will be explained in the following section from absorption data at 2650 A for compounds assumed to be typical of each of the two types of components that have characteristic absorption at that wavelength. The wavelength 2650 A was chosen to favor absorption by various alkyl substituted benzenes as much as possible relative to absorption by alkylnaphthalenes and other types of dicyclic aromatic. Probably any particular wavelength between 2650 and 2690 A would serve the purpose as well.

Evaluation of Average Specific Extinctions

The data used for the evaluation of an average specific extinction k_1 are given in figure 1. The line drawn for k_1 in figure 1 is the one of three tried for the spectrophotometric data on the 10 fuels, which gave results for total aromatics in best agreement with the accepted Bartlesville data. The points plotted in this figure indicate that the specific extinction is lower for the higher-boiling alkyl naphthalene compounds. In order to assign definite values to k_1 , some characteristic distillation temperature in the upper boiling range of a cut must be selected. The line in figure 1 is drawn to represent average characteristic values of k_1 as a function of the A.S.T.M. end point of a cut because this temperature is most often available. The location of this line is somewhat arbitrary and reflects some conditions characteristic of the experimental fuels investigated.

Several variable factors affect the location of the line in figure 1. The efficiency of the still used to obtain the cuts to be analyzed, the variation of concentration of condensed dicyclics present as a function of their boiling points, and the width of cut analyzed all have relatively significant effects on the probable value of k_1 in any particular case. General predictions of the probable values of k_1 to be applied in the case of particular refinery cuts may vary considerably and would probably lie within a band of values varying as much as ± 10 units from the line given.

The ultraviolet spectra of Midway fuel 3A (end point $390^\circ \text{F} \approx 200^\circ \text{C}$) and Hastings 5B (end point $400^\circ \text{F} \approx 204^\circ \text{C}$) showed well-resolved peaks at 3111 and 3192 Å, respectively, characteristic of naphthalene and monosubstituted naphthalenes. (See reference 3.) The magnitude of these peaks indicated that the concentrations of these two types of condensed dicyclics were approximately equal; therefore the still used to obtain the cuts was not very efficient otherwise such quantities of monosubstituted naphthalenes would not distill at approximately 30° to 50°C below their boiling points.

This spectrophotometric evidence was interpreted as justifying the values of k_1 (between the empirical points 189 (naphthalene) and 150 (methylnaphthalenes)) that are indicated by the line in figure 1 for end points in the range from 200° to 250°C . If a very efficient still were used, a line for k_1 drawn through 189 at 200°C and through 125 at 350°C would probably represent average conditions better.

The position of the k_1 line in the range from 240° to 350° C is also dependent upon the width of the cut to be analyzed as this width affects the ratio of lower-boiling to higher-boiling dicyclics in the cut. The cuts investigated were more than 100° C wide and this fact together with the low efficiency of the still probably resulted in the inclusion of all dicyclics that had boiling points below the end points of the cuts. For this reason the k_1 line is drawn considerably above the values measured on technical-grade compounds for end points above 240° C. For narrower cuts the k_1 line should be lower for the higher end points as was suggested in the previous paragraph for the case of a very efficient still.

Values of k_2 for several monocyclic aromatics given in figure 2 do not vary in a regular manner with boiling points of the compounds. Actually, the structure of the molecules is known to be the factor that affects both k_1 and k_2 . In spectra of the homologous series of monocyclic aromatics substitutions in the para positions yield large values for k_2 but substitutions in other positions yield smaller values. Although the correct value of k_2 is different for each cut and depends on the concentrations of respective monocyclic aromatics present, an average of the values in figure 2 (8.0) has been computed and arbitrarily applied. Agreement of estimates of total aromatics in 10 cuts based on this arbitrary average with values for total aromatics in the same cuts obtained by an accepted method has been used as a criterion for judging the reliability of this procedure.

RESULTS

Some data characterizing the 10 experimental jet-propulsion fuels, which boil in the range from 100° to 700° F, together with determinations of the alkylnaphthalene and total aromatic content by the spectrophotometric methods described herein are presented as percentage by volume of total sample in table I for comparison with similar Bartlesville data. Total aromaticity was determined at the Bureau of Mines Bartlesville laboratory by a silica-gel adsorption technique and alkylnaphthalene content was evaluated on the basis of the refractivity intercept of the aromatic extract. These methods have been described in a communication from the Bartlesville laboratory. The percentages of other aromatics, which consist largely of monocyclics plus some noncondensed dicyclic aromatics, if they are present, may be obtained from the data of either laboratory by subtracting the percentage of alkylnaphthalenes from the percentage of total aromatics.

DISCUSSION OF RESULTS

Because the analytical data presented in table I were obtained by two independent methods, they afford a basis for consideration of reliability, particularly for the spectrophotometric estimates of alkylnaphthalenic content.

Alkylnaphthalene Content of Fuels

The agreement of values for alkylnaphthalenic percentages is probably within the experimental errors of the methods in all cases but one. The maximum error possible in the spectrometric method was admitted to be large in reference 3 but usually dependent upon the amount of alkylnaphthalenes present. Consequently, the absolute magnitude of the error decreases as the concentration of alkylnaphthalenes becomes smaller and the method is especially suitable for relatively low concentrations. Evidence that indicates better reliability of the spectrometric method than was expected is presented in this discussion.

The refractivity intercept method proposed and applied at the Petroleum Experiment Station, Bartlesville, determines alkylnaphthalenic percentage in the aromatic extract of a cut from 0 to 100 percent in proportion as the refractivity intercept of the extract increases from 1.061 to 1.099 or 0.038. The formula for this percentage is

$$V_N = 100 \frac{R_T - 1.061}{1.099 - 1.061}$$

where V_N is the percentage of alkylnaphthalenes in the aromatic fraction and R_T is the refractivity intercept of the aromatic fraction. An analysis for low concentrations of dicyclics is dependent on the monocyclic aromatics present in the following way: If all the monocyclic aromatics have positive average deviation, which according to information from the Bartlesville Petroleum Experiment Station, is +0.0034 from the mean refractivity intercept 1.061, 9 percent of the aromatic fraction or 2.3 percent of a fuel that contained 25 percent total aromatics would be reported as alkylnaphthalenes although none was present. Conversely, if all the monocyclic aromatics had a negative average deviation of the same magnitude, the presence of as much as 9 percent alkylnaphthalenes in the aromatic extract or about 2.3 percent in a cut containing 25 percent aromatics would not be detected and would be reported as zero. This method therefore appears to be rather

unreliable for the determination of low alkyl-naphthalenic concentrations in a cut because the result is dependent to some extent on the monocyclic aromatics present. The average deviation of 0.0064 for alkyl-naphthalenes from their mean refractivity intercept 1.099 is also a source of error but the error becomes serious only in unusual cases of high concentrations of alkyl-naphthalenes. The foregoing considerations together with a probable error formerly believed to be about 15 percent of the amount present in the spectrometric determinations are adequate to account for all differences in the values for alkyl-naphthalenes except in the case of the high-boiling (370° to 630° F) cut of the Midway crude (NACA fuel number 45-623). The spectrophotometric procedure has been repeated and checked for this sample and the data at two wavelengths together with the NACA value for alkyl-naphthalenes give an estimate for total aromatics that is correct according to the main assumption in this report; hence, this difference has not been explained and is being investigated further.

Total Aromatic Content of Fuels

In the present discussion the percentages of total aromatics obtained at the Petroleum Experiment Station, Bartlesville, by silica-gel extraction are assumed to be correct, that is, the small inaccuracies, which doubtless exist, are neglected. The absorption by alkyl-naphthalenic aromatics at 2650 Å, where monocyclic aromatics have characteristic absorption, is about 18 times as intense as the monocyclic aromatic absorption. This fact means that a change of 1 percent in the concentration of alkyl-naphthalenes causes a change of approximately 18 percent in the spectrophotometric estimation of total aromatics. For this reason agreement of spectrophotometric estimates of total aromatics with values obtained by an accepted method constitutes a sensitive test of the accuracy of the estimate of alkyl-naphthalenes. For 8 of the 10 cuts the spectrophotometric estimate of total aromatic content deviated from the values determined by silica-gel extraction by an average of 0.8 percent, the largest being 1.9 percent. The close agreement of these values is evidence that the spectrophotometric methods of analysis used are applicable to the cuts of Bradford, Midway, Yates, and Hastings crudes with an average error of less than 0.05 percent in the determination of the alkyl-naphthalenes and less than 1 percent in the estimation of total aromatic content. Neither errors greater in value than these nor the presence of as much as about 0.5 percent of noncondensed dicyclics would have permitted the agreement found in the case of the eight cuts. The average error in the estimates of alkyl-naphthalenes determined in the same manner and averaged for all 10 cases was less than 0.2 percent.

Possible explanations of the difference of 5.7 percent for total aromatics in the gasoline fraction and of 14.5 percent in the kerosene fraction of the Tomball crude, which has the highest aromatic content of all the crudes, will be given subsequent to the following consideration of spectrophotometric interference.

Problem of Spectrometric Interference

A preliminary consideration of possible effects of absorption by certain compounds, the presence of which in appreciable concentrations is doubtful, has been given for the alkylnaphthalene region of 3100 to 3300 Å (reference 3, pp. 4 to 5). In addition, the same problem for the 2600 to 2700 Å region must be considered here. Some approximate specific extinctions at 2650 Å that may be compared with the value of k_2 (8.0) characteristic of alkylbenzenes are listed in the following table:

Number	Aromatic compound	Boiling point (°C)	Specific extinction k_1	Volume (percent)
1	Tetralin	207	31	2.9
2	Biphenyl	255	210	25.0
3	Diphenylmethane	262	13	0.6
4	1,1-Diphenylethane	272	12	.5
5	Bibenzyl	284	8	0
6	Anthracene	342	360	45.0
7	m-Diphenylbenzene	363	360	45.0

These values are the results of measurements on samples believed to be 95 or more percent pure. By analogy with homologous series of alkylbenzenes and alkylnaphthalenes, the alkyl homologs of the above types of aromatic may be expected to have specific extinctions of the same order of magnitude within a factor of two. On the assumption that if they are present the seven compounds in the tabulation should be included in a value for total aromatics, the presence of any one to the extent of 1 percent of a fuel would cause the spectrophotometric estimate of total aromatics to be high by approximately the percentage in the tabulation.

With the exception of tetralin, the presence of any of the previously listed compounds in kerosenes or Diesel oils has not been reported by any sources known to the authors but this fact may be due as much to the lack of analytical methods suitable for detecting low concentrations of these compounds as it is to the

complete absence of these compounds in natural crudes. In the case of 8 of the 10 fuels the close agreement of spectrophotometric estimates of total aromatics with values assumed to be correct makes the presence in the fuels of as much as 1 percent of tetralin or 0.1 percent of compounds 2, 6, or 7 improbable because the presence of these amounts would have caused the spectrophotometric estimates of total aromatics to be high by approximately 3 percent. By the same reasoning the spectrophotometric estimates of total aromatics in the cuts of the Tomball crude, which were high by 5.7 and 14.5 percent, could be attributed to the presence of two and three times, respectively, the aforementioned amount of any one of the compounds or to a suitable combination of these compounds in smaller amounts. This explanation for the high values for total aromatics in both cuts of the Tomball crude is probably preferable to the possibility that the high values are due to estimates of alkylnaphthalenes low by about 0.3 and 0.8 percent in cuts 1A and 1B, respectively.

SUMMARY OF RESULTS

From ultraviolet spectrophotometric measurements on typical alkylnaphthalenic compounds and on the 10 experimental jet-propulsion fuels used for this investigation, the following results are obtained:

The characteristic ultraviolet absorption by alkylnaphthalenes is such that in the application of spectrophotometric methods of estimation a change of 1 percent in the amount of these compounds caused a change of approximately 18 percent in the estimated total aromatic content.

The fact that if all differences between values for total aromatics determined by two methods were attributed to errors in the spectrophotometric estimation of alkylnaphthalenes, the average of these errors was less than 0.2 percent, or for eight cuts not including the Tomball crude the average was 0.05 percent, was evidence of unexpected reliability of the spectrophotometric method when applied to these crudes. However, a difference between spectrophotometric and refractivity intercept values for alkylnaphthalenes in the high-boiling cut of the Midway crude has not been explained.

Spectrophotometric methods in conjunction with an accepted method evaluating total aromatic content of a kerosene-like fraction show promise of indicating the presence of more than

about 0.2 percent of noncondensed conjugated dicyclic aromatics of the diphenyl type. The possibility of undetectable interference, however, prevents proposal of ultraviolet estimation of total aromatics as an independent method except in particular cases.

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2. Mair, Beveridge J.: Separation and Determination of Aromatic and Monocolefin Hydrocarbons in Mixtures with Paraffins and Naphthenes by Adsorption. Res. Paper 1652, Nat. Bur. Standards Jour. Res., vol. 34, no. 5, May 1945, pp. 435-451.
3. Cleaves, Alden P., and Carver, Mildred S.: A Spectrophotometric Method for Identification and Estimation of Alkyl-naphthalenic-Type Hydrocarbons in Kerosene. NACA TN No. , 1947.
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TABLE I - PERCENTAGE BY VOLUME OF AROMATICS IN 10 JET-PROPULSION FUELS

THAT ARE CUTS FROM FIVE CRUDES

Bureau of Mines Crude	YATES	HASTINGS			TOMBALL		BRADFORD		MIDWAY	
	4A	5A	5B	5C	1A	1B	2A	2B	3A	3B
NACA fuel	45-667	45-668	45-669	45-670	45-657	45-659	45-627	45-626	45-622	45-623
Approximate boiling range A.S.T.M. (°F)	160 340	120 310	280 400	410 690	210 340	400 590	90 360	340 540	110 390	370 630
NACA alkyl- naphthalenes	0.16	0.012	0.6	0.7	0.02	12.6	0.01	1.11	0.20	10.0
Bureau of Mines alkylnaphtha- lenes (percent)	0	0	1.9	2.3	0	11.5	0	0	0	0.20
NACA total aromatics	5.3	4.1	17.2	23.2	37.0	46.7	8.1	13.1	9.6	34.3
Bureau of Mines total aromatics (percent)	5.9	5.3	16.8	25.1	31.3	32.2	7.5	12.4	9.7	33.2
Difference	-0.6	-1.2	0.4	-1.9	5.7	14.5	0.6	0.7	-0.1	1.1

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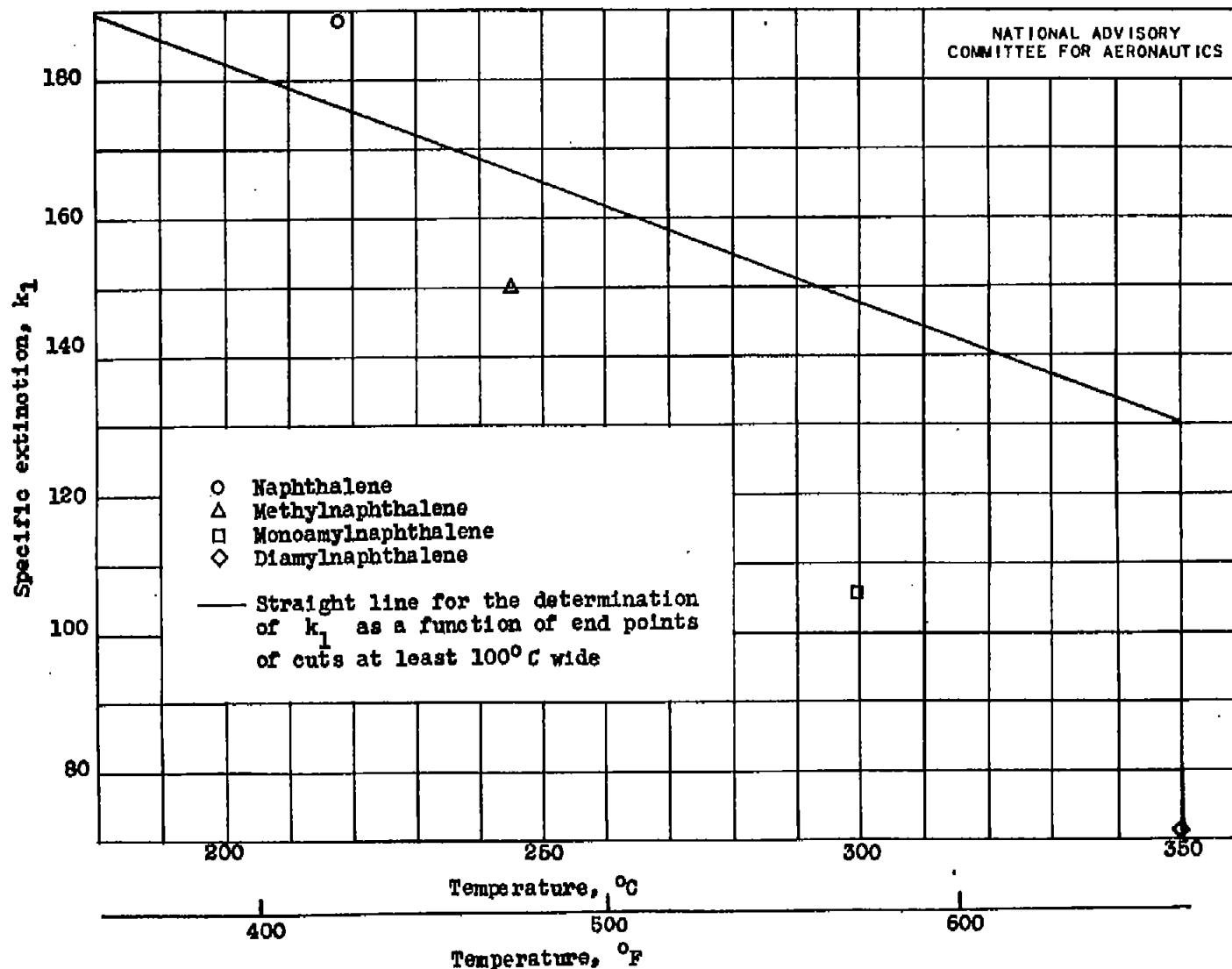


Figure 1. - Specific extinction k_1 of alkyl naphthalenes at 2650 Å plotted at boiling points of the aromatics. Solution, 1 percent by volume; cell thickness, 0.5 centimeter.

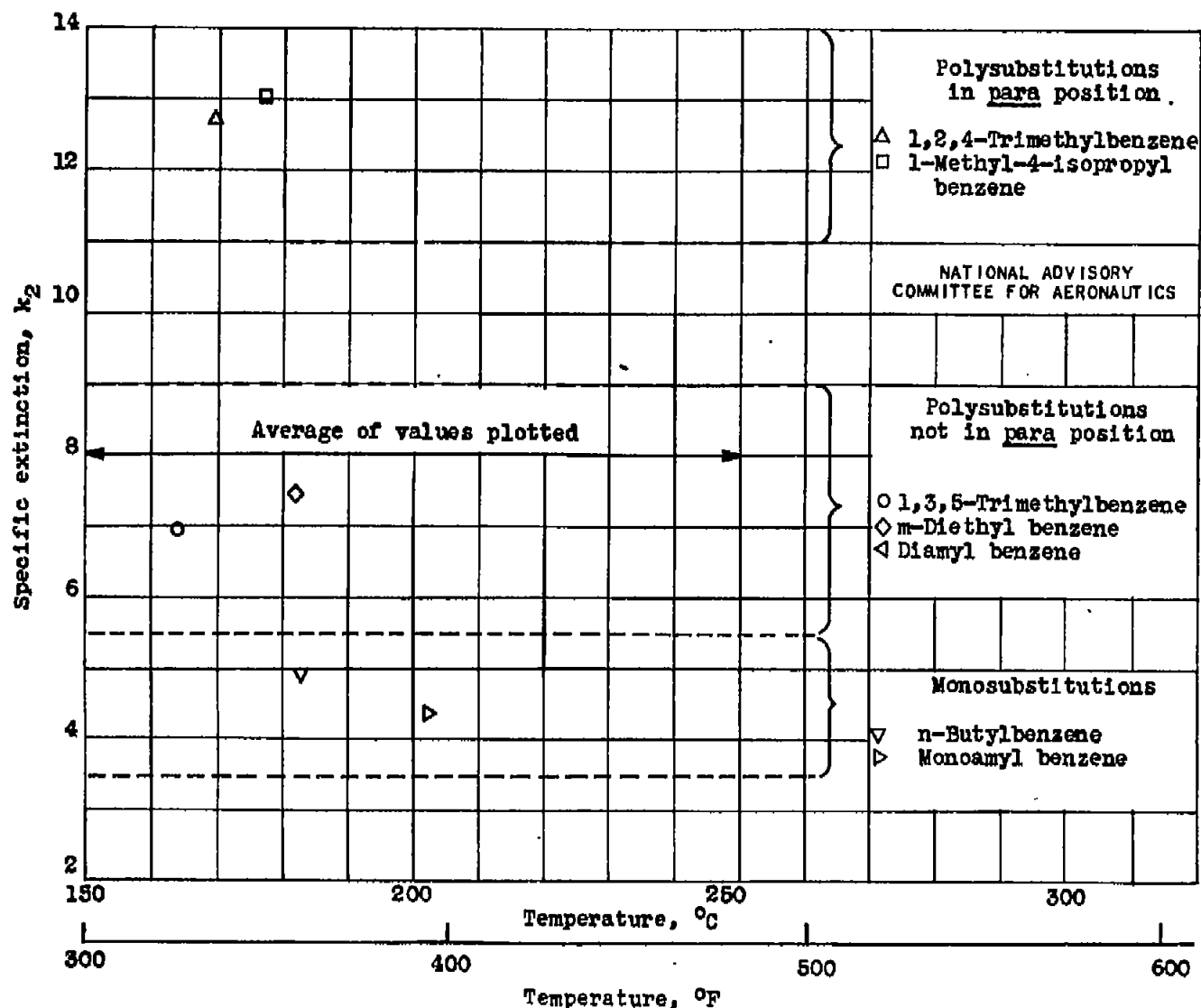


Figure 2. - Specific extinction k_2 of alkyl benzenes at 2650 Å plotted at boiling points of the aromatics. Solution, 1 percent by volume; cell thickness, 0.5 centimeter.

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